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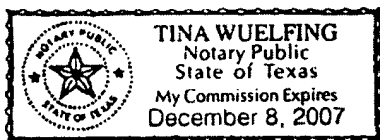
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METHOD FOR THE ANODIC ALKOXYLATION OF ORGANIC SUBSTRATES

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(57) Abstract: Organic substrates, such as cyclic ethers, N-substituted amides, ketones, alkyl-aromatic substances and alkyl-heteroaromatic substances can be anodically alkoxyated, especially methoxylated, in the presence of an alcohol. Alkoxylation in the presence of a mediator or in a divided cell using a solid electrolyte is known. The anodic alkoxylation according to the invention is carried out in the absence of a mediator in an undivided electrolytic cell using a diamond anode or gold anode and allows for high yields and a high current efficiency.

The subject matter of the present invention relates to a method for the anodic alkoxylation of organic substrates, in particular cyclic ethers, such as especially furan and furan derivatives, which may also be wholly or partially hydrogenated, N-substituted amides, carbonyl compounds, alkyl aromatic hydrocarbons and alkyl heteroaromatic hydrocarbons. The anodic alkoxylation, more specifically the methoxylation, is carried out in an unpartitioned electrolytic cell in the absence of a solid polymer electrolyte.

Alkoxylation reactions of saturated and unsaturated cyclic ethers and of N-alkyl amides and alkyl aromatic hydrocarbons and alkyl heteroaromatic hydrocarbons are of industrial importance since the resulting products or the hydrolysis products thereof are valuable raw materials for pharmaceuticals and pesticides. Several different methods for the anodic alkoxylation of organic compounds are known.

U.S. Patent 2,714,576, for example, discloses the electrolytic production of 2,5-dialkoxy-2,5-dihydrofurans during which furan or a substituted furan is electrolyzed in an aliphatic alcohol with 1-5 carbon atoms in the presence of a soluble electrolyte. The electrolyte used is ammonium bromide, the effect of which is to act as a mediator. The substrate to be alkoxyated thus is alkoxyated not directly but indirectly via the intermediate step of a bromination. Instead of ammonium bromide, other halogen compounds can be used as a supporting electrolyte salt and a mediator as well. A serious drawback of the anodic alkoxylation in the presence of a mediator, such as especially a halogen compound, is that the mediator itself can lead to an increased formation of by-products and thus makes the processing and purification of the alkoxyated substrate more difficult. Undesirable halogenated by-products are formed especially when halogen compounds are used as a mediator.

As is disclosed by GB Patent No. 731,116, furan derivatives can also be anodically alkoxylation in the presence of supporting electrolyte salts which do not act as a mediator, such as concentrated sulfuric acid, boron fluoride etherate, sodium formate and sodium nitrate. A serious drawback of an anodic alkoxylation without a mediator is that only very low current efficiencies and product yields can be obtained, with the values in most cases being markedly lower than 50%.

The anodic methoxylation of furans in a methanolic sodium acetate solution or a methanolic sodium methylate solution has been described by A. J. Baggaley and R. Brett in J. Chem. Soc. (C), 1968, pp. 969-974. Under the electrolysis conditions selected, the targeted product 2,5-dihydro-2,5-dimethoxyfuran was obtained in an only very low yield.

Although the previously discussed methods are always carried out in an unpartitioned electrolytic cell, it is also possible to carry out electrochemical alkoxylation in an electrolytic cell that is partitioned by an ion exchange membrane, for example, reference is made to the U.S. Patent No. 5,074,974.

In the embodiment described in that document, a catholyte and an anolyte are passed through the partitioned electrolytic cell, with the anolyte used being the catholyte from a previous reduction. Although this method makes it possible to produce purer alkoxylation products, the degree of technical complexity is considerably greater than during the alkoxylation in an unpartitioned electrolyte cell.

In an effort to further improve the alkoxylation of organic substrates, such as furans and N-alkyl amides, methods have been developed which can be carried out without conductivity-increasing additives but which instead use a solid polymer electrolyte (solid polymer electrolyte = SPE). As an example, reference is made to the article by R. Fabiunke and J. Jörissen in Chem.-Inf.-Tech. 62 (1990), No. 5, pp. 400-403. By methoxylating furan using a Nafion® membrane (polyfluorinated sulfonated resin), it is possible to obtain high product yields of dimethoxydihydrofuran as long as the water content is low. The disadvantage is that a high cell voltage is required. Although an increase in the temperature makes it possible to reduce the cell voltage and thus to increase the current efficiency, this type of approach is not useful since the chemical stability of the methoxy compound is extremely limited. The cell voltage can also be reduced by reducing the thickness of the membrane but this has the effect that the mechanical vulnerability of the membrane is considerably increased at the same time. Although the SPE method appears to be of interest to the anodic alkoxylation because of the absence of a supporting electrolyte salt, it has so far not been possible to develop this method as a viable economic alternative to the methods which operate in an unpartitioned electrolytic cell in the

presence of a mediator, in particular a halide. The low current efficiency of the SPE method is at least in part attributable to the destruction of the Nafion® membrane as a result of the by-products of the reaction. By adding a mediator, such as bromine or bromide, it is possible to increase the current efficiency and to reduce the voltage, except that the undesirable halogenated by-products must again be accepted as a tradeoff.

In German Patent No. DE 195 33 773 A1, a plate stack cell with in-series-connected stack electrodes is used for the electrolytic oxidation, including an anodic alkoxylation, with at least one stack electrode being a graphite felt plate, a carbon felt plate or a fabric of an educt contact surface covered with carbon. The electrodes and the electrolyte are designed to ensure that in the ideal case, no electrolyte ions migrate through the stack electrode. Preferably the electrolyte phase in contact with the carbon-containing stack electrode is a solid polymer electrolyte. The plate stack cell is technically extremely complex since the cell requires a specific configuration and a suitable periphery.

In the method described in German Patent No. DE 100 45 664 A1, mediators, such as are used for the electric oxidation and reduction of the most varied substrates, are regenerated electrochemically. The compound used as mediator is brought into contact with a diamond film electrode which causes an exchange of a redox equivalent to take place. The electrochemical regeneration is an oxidation or reduction of the compound used as a mediator, depending on whether the organic compound is to be reduced or oxidized by means of the mediator. Mediators to be mentioned are those of the series of the metal salts and halogen compounds that are available in a number of oxidation stages but also organic mediators. The method described in the document mentioned above is, among other things, suitable for the alkoxylation of carbonyl compounds, N-alkyl amides, alkyl aromatic hydrocarbons and heterocyclic compounds, such as furan and tetrahydrofuran and N-methyl pyrrolidone-2. The diamond film electrode to be used has a core comprising, for example, titanium, silicon or graphite, onto which a doped conducting diamond film is deposited.

Although the method described in the document mentioned above can be carried out both in a partitioned and an unpartitioned electrolytic cell, the inherent disadvantage is that a mediator must be used.

To obtain the conductivity required, diamond film electrodes are doped with a tri- to pentavalent element, such as in particular boron or phosphorus. As to the production of the diamond film electrodes, reference is made to German Patent No. DE 199 11 746 A1 as an example.

J. Iniesta et al. studied the electrochemical oxidation of 3-methylpyridine using a boron-doped diamond film electrode in an acid medium. Under electrolysis conditions with the

decomposition of water, a polymer film formed on the electrode surface; at a potential above the decomposition of water, indirect oxidation reactions as a result of the hydroxyl radical took place. An alkoxylation is not described in said document.

Thus, the problem to be solved by the present invention is to make available another method for the anodic alkoxylation, in particular methoxylation, of organic substrates, in particular of cyclic ethers and N-substituted amides, which method can be carried out in a simple manner and which can also be used for the industrial production of the alkoxyated products. The method to be disclosed was to have neither the disadvantages known from the SPE method nor should it lead to an alkoxylation product with halogenated by-products.

Surprisingly, it was found that a large number of organic substrates can be alkoxyated by carrying out the anodic alkoxylation using a diamond film anode or a gold anode in the absence of a mediator. It was not possible to anticipate that the alkoxylation according to the present invention can be implemented with a high current efficiency and a high product yield. Considering the teaching of German Patent No. DE 100 45 664 A1, this simple solution of the problem was surprising since the method described in said patent required that a mediator be used in all cases.

A special advantage of the invention is that it is not necessary to use a specially designed electrolytic cell to carry out the anodic oxidation, which makes it possible to use a simple electrode configuration. In addition, cell packages in a stacked configuration are possible.

Thus, the method for the anodic alkoxylation of an organic compound found provides that a mixture comprising the organic compound and a primary alcohol with 1-4 C atoms be alkoxyated in an unpartitioned electrolytic cell in the presence of a supporting electrolyte salt that is soluble in the mixture, but in the absence of a solid polymer electrolyte, at an effective cell voltage using an oxidation-resistant anode, which method is characterized in that the anodic alkoxylation is carried out in the absence of a mediator, using a diamond film anode or a gold anode.

The dependent claims relate to preferred embodiments of the method according to the present invention, including the substrates to be preferably alkoxyated and the supporting electrolyte salts to be preferably used, which salts, even in a low concentration, lead to an adequate conductivity and are not oxidizable under the electrolysis conditions, thus ensuring that they do not have the effect of a mediator.

Suitable for use in the anodic alkylation [sic; alkoxylation] are, in particular, organic compounds of the series of cyclic ethers, N-substituted amides, carbonyl compounds, alkyl aromatic hydrocarbons and alkyl heteroaromatic hydrocarbons.

The first group of substrates to be readily alkoxyated are cyclic ethers which can be saturated, unsaturated or heteroaromatic. The ring system containing oxygen preferably has 5-7 ring members, preferably 5 or 6 ring members with an O atom, but additional saturated or unsaturated ring systems, in particular benzene nuclei, can also be anellated to this ring system. Examples of substances of the groups mentioned are furan and mono- to tetra-substituted furans as well as the dihydro and tetrahydro compounds derived therefrom, such as tetrahydrofuran. Other cyclic ethers are 1,2- and 1,4-pyrans and the di- and tetrahydro derivatives thereof; 1,4-pyrones and the di- and tetrahydro derivatives thereof can also be anodically alkoxyated. In addition, 1,2-pyrones which are, however, lactams can be alkoxyated. The substituents are, in particular, alkyl groups which in turn can have a functional group, such as hydroxyl, acetoxy, alkoxy carbonyl, amidocarbonyl, carboxyalkyl, nitrile and amino. Preferably, such a functional group is bound to the heterocyclic ring via a methylene or ethylene bridge. Other substituents are alkoxy, halogen, carboxyl, acyl and the aldehyde groups. Nonaromatic cyclic ethers that are to be alkoxyated must have at least one abstractable H atom on a C atom that is next to an ether oxygen.

Using furan or a substituted furan, the anodic alkoxylation according to the present invention makes it possible to obtain the corresponding 2,5-dihydro-2,5-dialkoxyfurans with a generally high material yield and a very high current efficiency. Using the hydrogenated furans or other cyclic ethers, such as pyrans, pyrones, dioxane and morpholine as the starting materials, the corresponding mono- or/and dialkoxy derivatives are obtained, with the alkoxy groups being located on the carbon atom(s) next to the ether oxygen.

Using a different embodiment of the method according to the present invention, it is possible to alkoxyate linear and cyclic N-substituted amides. The amide nitrogen atom has one or two alkyl substituents which can also form a saturated or unsaturated, possibly heteroaromatic ring with the N atom. In this case, at least one C atom bound to the nitrogen has at least one abstractable hydrogen atom, or the nitrogen atom is a ring member of a heteroaromatic ring.

Examples of such amides are lactams with 5-7 ring members, with the possibility that the amide nitrogen can be additionally alkylated.

The lactams include, for example, N-alkyl pyrrolidone, with the possibility that the heterocyclic ring in addition has one or more substituents. Most preferably the alkyl group bound to the nitrogen is methyl. Other examples are N-alkyl valerolactam and N-alkyl caprolactam.

Another group of compounds are N-acylated saturated and unsaturated N-heterocyclic compounds which have at least one abstractable hydrogen atom on at least one of the carbon atoms next to the nitrogen or which are heteroaromatic. Examples of the previously mentioned groups are: N-acylated pyrroles, pyrrolines and pyrrolidines optionally mono- or polysubstituted

on the ring. The acyl group may be, for example, formyl, acetyl, propionyl or benzoyl. The substituents that are bound to one or more carbon atoms of the N-heterocyclic ring are substituents such as were listed above in connection with the cyclic ethers. Especially preferred substituents are an alkyl group with 1-4 C atoms, in particular methyl or ethyl, hydroxymethyl, acetoxymethyl and carboxymethyl.

It is also possible to alkoxylate open-chain N-alkyl or N,N-diallyl fatty acid amides, in particular amides of fatty acids with 1-6 carbon atoms. In addition, it is possible to use substrates which have two N-alkyl amide structural element in one molecule.

According to another embodiment, ketones with a methyl group or methylene group bound to the carbonyl carbon atom are alkoxylated, in particular methoxylated or ethoxylated. Examples include aliphatic ketones with 3-12 C atoms, aromatic-aliphatic ketones, such as acetophenone, and methyl benzyl ketone. The resulting alkoxy ketones are generally converted directly into the corresponding ketal.

According to another embodiment, alkylated aromatic and heteroaromatic compounds are alkoxylated, in which case the carbon atom of an alkyl group bound to the aromatic hydrocarbon or to the heteroaromatic hydrocarbon must have at least one abstractable hydrogen atom. The substrates can, in addition, have substituents other than alkyl. The aromatic or heteroaromatic hydrocarbon preferably has one or more alkyl groups of the series of methyl, ethyl and n-propyl. The alkoxylation according to the present invention leads to the corresponding alkoxy alkyl aromatic and heteroaromatic hydrocarbons.

In practice, during the alkoxylation, the substrate to be alkoxylated is dissolved using the alcohol that is used for the alkoxylation as the solvent. After the addition of an effective quantity of a supporting electrolyte salt, this solution is passed through the unpartitioned electrolytic cell. The reaction mixture obtained after adequate alkoxylation can be suitably processed by means of distillation and/or extraction. The bottom containing the supporting electrolyte salt is returned to the process. The anodic alkoxylation can be carried out by continuous or by batch operation.

The supporting electrolyte salt used is a substance, the ions of which are neither oxidized nor reduced in the range of the potential selected so that the supporting electrolyte salt does not act as a mediator and therefore undergoes, if any, only very insignificant secondary reactions. Especially preferred supporting electrolyte salts are tetraalkyl ammonium salts. The alkyl groups of the tetraalkyl ammonium ion are, in particular, alkyl with 1-6 C atoms, especially preferred are 3 or 4 C atoms. Two alkyl groups together with the ammonium nitrogen can jointly form a ring system, especially a five- or six-membered ring. Also usable are those tetraalkyl ammonium salts in which three alkyl groups form a bicyclic ring system.

The anions of the supporting electrolyte salts to be preferably used according to the present invention are preferably those of the series of ClO_4^- , BF_4^- , PF_6^- , SbF_6^- , R-SO_3^- and R-SO_4^- ; R here stands for an alkyl which can also be halogenated, especially CF_3- , CCl_3- or CF_3CH_2- , R can also stand for an aryl which in turn can be substituted as well. In principle, it is also possible to use other supporting electrolyte salts, for example, sulfates, nitrates, phosphates, phosphonates, carboxylates and alcoholates, but in most cases, the yields from these are lower than the yields obtained with the use of the preferably used supporting electrolyte salts mentioned above. According to an especially preferred embodiment, the supporting electrolyte salt used is tetra-n-butyl ammonium tetrafluoroborate.

Since the supporting electrolyte salts are essentially completely inert under the electrolysis conditions, no secondary reactions take place, and, in addition, these supporting electrolyte salts can also be separated very easily. The quantity of the supporting electrolyte salts used ... [bottom line cut off] ... an adequate conductivity of the solution to be electrolyzed is reached. The quantity of the supporting electrolyte salt used is generally in a range from 0.1-5 wt%, preferably from 0.3-3 wt%, relative to the solution to be electrolyzed.

The anodic oxidation is generally carried out at a voltage in a range from 1-70 volt, in particular from 5-25 V. The current density is preferably set to a range from 1-25 A/dm^2 ; however, values below as well as above the threshold values are also possible.

The anode is one with a diamond film. The substrate material for the diamond film is preferably a material of the of graphite, graphite/gold, silicon or a passivating metal, such as titanium, zirconium, niobium, tantalum, tungsten and molybdenum, or a carbide or nitride of the elements Ti, Si, Nb, Ta, Zr and Mo.

The material to be used for the cathode is one that is stable in the reaction medium. Especially suitable is a material of the series of graphite, platinum nickel, stainless steel and diamond film if the reaction medium is substantially anhydrous. When aqueous media are to be electrolyzed, a cathode material with a high hydrogen or oxygen overvoltage is to be preferred; i.e., preferably a diamond film electrode is used.

As the examples and reference examples below will show, the current efficiencies obtained with the use of a diamond film electrode, in particular a boron-doped diamond film electrode, in the anodic alkoxylation in an unpartitioned electrolytic cell in the absence of a mediator are considerably higher than those obtained with the use of the prior-art electrodes.

In the section describing the examples, a few material yields and current efficiencies obtained during the methoxylation of furan without a mediator are listed, which values can be found in the prior art or can be calculated. In contrast to the very low efficiencies in the prior art, using the method according to the present invention to methoxylate furan at an electrolyte

temperature in a range from 15-20°C makes it possible to obtain nearly quantitative current efficiencies with a charge conversion efficiency of approximately 75%.

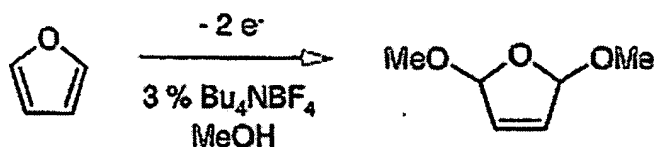
All diamond film electrodes presently known can be used in the method according to the present invention. Diamond film electrodes which are rendered conductive by means of a suitable dopant are highly corrosion-resistant and significantly less susceptible to electrode fouling. Based on experiences so far, in contrast to other electrodes, the diamond film electrodes to be used have not undergone any adsorption phenomena which could reduce the selectivity. Similarly good results are obtained with a gold anode. As already discussed earlier, the absence of a mediator makes it easier to process the electrolyte product. At the same time, the purity of the alkoxylation product is higher since by-products that can form as a result of the mediators, including products of a reaction between the substrate or the alkoxylation product and the mediator, are absent.

The configuration of an electrolysis system to be used is known in the art. The cathode can be made of conventional materials, but it can also be a diamond film electrode.

The present invention will be explained in greater detail based on the following examples and reference examples.

Example B1

Direct methoxylation of furan on a boron-doped diamond film anode



A methanolic furan solution (furan concentration 8 wt%; molar ratio of methanol:furan 24:1) was used. The volumetric flow rate through the electrolytic cell was 1 L/min.

Under galvanostatic conditions (100 mA/cm²) at an average electrolyte temperature of 15°C and a charge consumption of 1.52 F/mol (76% of the theoretical), the anodic conversion of furan in methanol with Bu₄NBF₄ (3%) (as the supporting electrolyte salt) in an unpartitioned electrolytic cell (flow-type cell, electrode spacing 4 mm) led to the following yields of 2,5-dihydro-2,5-dimethoxyfuran which were determined by means of calibrated HPLC:

Current efficiency	=	99%
Material yield	=	75%

As the reaction continued up to a charge consumption of 2.28 F/mol (114% of the theoretical), the current efficiency dropped to 74%. As was to be expected, the material yield

increased and measured 84%. For the analysis, commercially available 2,5-dihydroxy-2,5-dimethoxyfuran was used as the reference substance. The raw electrolyte product produced was colorless and water-white.

Example B2

Direct methoxylation of furan on a diamond film anode in the presence of Na methylate as the supporting electrolyte salt

Under galvanostatic conditions (100 mA/cm²) at an average electrolyte temperature of 17°C and a charge consumption of 66% of the theoretical, the anodic conversion of furan in methanol with MeONa (0.5%) (as the supporting electrolyte salt) in an unpartitioned electrolytic cell (flow-type cell, electrode spacing 4 mm) led to the following yields of 2,5-dihydro-2,5-dimethoxyfuran which were determined by means of calibrated HPLC:

Currency efficiency = 82%

Material yield = 58%

The raw electrolyte product produced had a light yellowish color and was clear. The anodic methoxylation of furan in the presence of sodium methylate has the advantage that a supporting electrolyte salt, the anion of which corresponds to that of the alkoxylation agent, can be used. The tradeoff for this advantage, however, is a lower material yield. Although a higher yield is obtained with a supporting electrolyte salt of the type according to Example B1, the use of an alkoxylate as the supporting electrolyte salt and a diamond film electrode still results in a material yield that is more than twice as high than that obtained with the use of an alkoxide and a platinum anode (see literature citation C).

Example B3 and Reference Example VB1

In Table 1 below, in addition to the results of Examples B1 and B2, the results of another example (B3) according to the present invention and of a reference example (VB1) for the methoxylation of furan are listed. The electrolytic solution of Example B3 and Reference Example VB1 contained 7-8 wt% of furan in methanol and 3 wt% of the supporting electrolyte salt; in B3 and VB1, the anode was different. Surprisingly, the results obtained with the gold anode were similarly good as the results obtained with a diamond film anode. In contrast, a graphite anode led to a considerably lower current efficiency.

①	②	③	Table 1		④	⑤	⑥
Nr.	Anode/ Kathode	Leit- salz	T [°C]	U [V]	Ladungs- Umsatz [%]	Strom- ausbeute [%]	Material ausbeute [%]
B1	Dia/Dia	Bu ₄ NBF ₄	15*	22-24	76	99	75
					114	74	84
B2	Dia/Dia	NaOMe	17*	27-29	66	82	58
B3	Au/Dia	Bu ₄ NBF ₄	16*	19-21	76	95	72
VB1	Gr/Dia	Bu ₄ NBF ₄	13*	20-21	79	69	54

Dia = boron-doped diamond film electrode

* = average temperature

Gr = graphite

- Key:
- 1 No.
 - 2 Anode/cathode
 - 3 Supporting electrolyte salt
 - 4 Charge consumption (%)
 - 5 Current efficiency (%)
 - 6 Material yield (%)

Reference Example VB2

Mediator-mediated (NaBr) methoxylation of furan on a diamond film anode

Under galvanostatic conditions (100 mA/cm²) at an average electrolyte temperature of 15°C and a charge consumption of 76% of the theoretical, the anodic conversion of a mixture of furan (8 wt%), methanol and NaBr (0.9 wt%) as the mediator and supporting electrolyte salt in an unpartitioned electrolytic cell (flow-type cell, electrode spacing 4 mm) led to the following yields of 2,5-dihydro-2,5-dimethoxyfuran which were determined by means of calibrated HPLC:

Current efficiency = 77%

Material yield = 59%

The crude electrolyte product produced in Reference Example VB2 had a yellowish orange color and was clear.

Reference Examples VB3 to VB8

The data listed in Table 2 were taken from literature citations A), B) and C).

①	②	③	Table 2						⑦
Nr. VB	Anode/ Kathode	Leit- salz	T [°C]	U [V]	Ladungs- Umsatz [%]	Strom- Ausb. [%]	Mat.- Ausb. [%]	Lit.	
3	n.a.	NH ₄ NO ₃	-10	5.8-6.8	100	(40)	40	B	
4	n.a.	NaNO ₃	-15*	5	90	43	39	A	
5	n.a.	NaO ₂ CH	-14*	7.0-8.8	100	(38)	38	B	
6	n.a.	BF ₃ Et ₂ O	n.a.	n.a.	74	45	33	A	
7	n.a.	H ₂ SO ₄	n.a.	n.a.	53	41	22	A	
8	Pt/Hg	NaOAc	21*	14-100	n.a.	n.a.	24	C	

n.a. = not specified

* = average temperature values

(xx%) = calculated current efficiency

A) = N. Clauson-Kaas, British Patent No. GB 731116 (1955)

B) = N. Clauson-Kaas and Z. Tyle, Acta Chem. Scand. 1952, 6, pp. 962-963.

C) = J. Baggaley and R. Brett, J. Chem. Soc. (C) 1968, pp. 969-974. Description of the electrolytic cell used by Baggaley in: D.-N. Nguyen, Acta Chem. Scand. 1958, 12 (3), p. 585-586.

Key: 1 No.
2 Anode/cathode
3 Supporting electrolyte salt
4 Charge consumption (%)
5 Current efficiency (%)
6 Material yield (%)
7 Literature citation

The currency efficiency and the material yield of the tests listed in Table 2 and carried out under prior-art conditions are considerably lower than those obtained in the tests according to Examples B1 to B3 which were carried out under the conditions according to the present invention. This illustrates the unexpectedly high positive influence of the choice of anode.